



Photooxidation of *N*-acylhydrazones to 1,3,4-oxadiazoles catalyzed by heterogeneous visible-light-active carbon nitride semiconductor

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ABSTRACT

The remarkable bioactivity of 1,3,4-oxadiazoles permanently motivates chemists to develop new milder and broader approaches to synthesize new derivatives, as well as to improve the preparation methodologies of the known compounds. Potassium poly(heptazine imide), a well crystallized representative of carbon nitrides family, shows great performance as a heterogeneous and hence recyclable photocatalyst in the visible light driven oxidative cyclization of *N*-acylhydrazones to the corresponding oxadiazoles. The proposed method uses elemental sulfur as a cheap and selective electron scavenger. A series of 2,5-disubstituted-1,3,4-oxadiazoles bearing aryl, hetaryl and alkyl substituents were obtained with 42–84% isolated yield.

1. Introduction

Visible light driven photocatalytic reactions are considered as a powerful tool to solve a wide variety of challenges in the modern organic synthesis. Transition metal complexes [1–4] and organic dyes [5–9] currently take the main role among homogeneous photocatalysts, the successful systems possessing an enhanced lifetime of the excited state and high quantum efficiency. However, these homogeneous photocatalysts are often associated with high cost, difficulties of separation from the reaction mixture, and thereby problems of reuse. This problem can be solved using heterogeneous photocatalysts such as carbon nitride materials. On the one hand, these materials already showed their efficacy in water splitting [10], carbon dioxide reduction [11], as well as in diverse organic transformations under visible light irradiation [12,13]. On the other hand, this catalysts family comes with low price and simplicity in preparation, and their high stability and reusability make them nicely complement to homogeneous photocatalysts.

A new version of the carbon nitride concept, potassium poly(heptazine imides) (K-PHI), was recently discovered [14–17]. Unlike polymeric covalent carbon nitride, K-PHI has charged nitrogen atoms and K^+ as counter ions and thereby crystallizes more easily. Due to this structural peculiarity, the valence band position becomes significantly more positive (+2.6 eV vs. RHE) (Fig. 1). K-PHI is highly effective for different photooxidation processes such as oxygen evolution reaction [18], oxidation of alcohols followed by Hantzsch pyridine synthesis [19].

It is hard to overestimate the value of oxadiazole core for the medicinal chemistry since its derivatives possess anti-inflammatory

[20], antimycobacterial [21], anticancer [22] and antiretroviral (raltegravir) [23] activities. Oxidative cyclization of *N*-acylhydrazones (Scheme 1) is one of the general synthetic methods of 1,3,4-oxadiazoles preparation. However, this synthetic approach requires strong oxidants such as bis(trifluoroacetoxy)iodobenzene [24], the Dess-Martin reagent [25], $Bu_4N^+I^-/t\text{-BuOOH}$ [26], I_2/H_2O_2 [27], $Cu(OTf)_2$ [28] or Iron (III)/TEMPO [29]. All these methods unavoidably are burdened with significant amounts of byproducts, which are created along with the target oxadiazole and should be removed in a proper manner. This is a problem especially on a large scale. On the contrary, oxidative cyclization of *N*-acylhydrazones to 1,3,4-oxadiazoles catalyzed by Eosin Y using O_2 as a gratuitous electron scavenger was reported [30], thus already indicating the possibilities of photochemistry as an effective method to enable organic synthesis without producing solid wastes. However, recycling of the photocatalyst still remains a challenge.

In this work, we present a new method of 1,3,4-oxadiazoles synthesis from *N*-acylhydrazones under visible light irradiation using K-PHI as a reusable heterogeneous photocatalyst and elemental sulfur (S_8) as a cheap and convenient electron scavenger. The developed protocol smoothly furnishes the target 1,3,4-oxadiazoles with high selectivity, while no solid byproducts are generated.

2. Experimental section

2.1. Materials

All starting materials were purchased from commercial sources. All reactions were carried out under an argon atmosphere. Analytical thin

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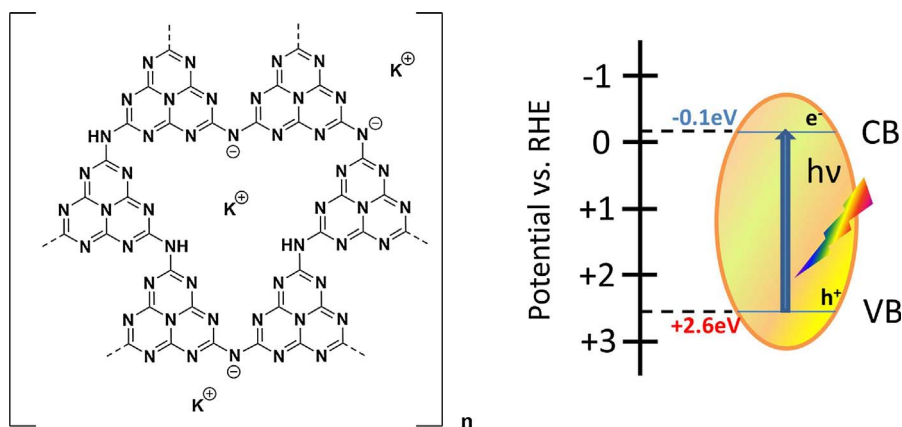
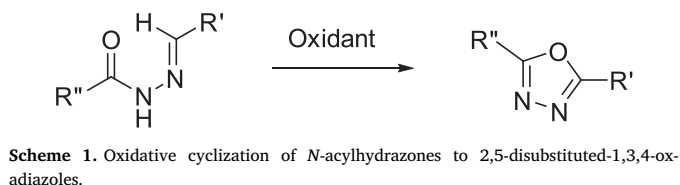


Fig. 1. Molecular (a) and band (b) structures of K-PHI.



layer chromatography (TLC) was performed on POLYGRAM SIL G/UV254 sheets and visualized with 254 nm light. Purification of compounds was carried out on Fluka Silica gel 60 (0.035–0.07 mm).

2.2. Synthesis procedures

2.2.1. Potassium poly(heptazine imide) (K-PHI)

Potassium poly(heptazine imide) (K-PHI) was synthesized according to the previously described procedure [19]. Mixture of lithium chloride (3.71 g), potassium chloride (4.54 g) and 5-aminotetrazole (1.65 g) was grinded in ball mill for 5 min at the shaking rate 25 s^{-1} . Reaction mixtures were transferred into porcelain crucibles and covered with lids. Crucibles were placed in the oven and heated under constant nitrogen flow (15 L min^{-1}) and atmospheric pressure at a following temperature regime: heating from room temperature to 550°C for 4 h, annealing at 550°C for 4 h. After completion of the heating program, the crucibles were allowed to cool slowly to room temperature under nitrogen flow. The crude products were removed from the crucibles, washed with deionized water (100 mL) for 3 h in order to remove salts, then filtered, extensively washed with deionized water and dried in a vacuum oven (20 mbar) at 50°C for 15 h. Characterization data of K-PHI (PXRD patterns, XPS, UV–vis and PL spectra, SEM and AC-HRTEM images) are shown in Fig. 2.

2.2.2. General method for preparation of *N*-acylhydrazones (1a–l)

To a solution of benzhydrazide (or nicotinohydrazide) (2.2 mmol) in 10 mL of methanol, aldehyde (2.2 mmol) was added and resulted solution was stirred at 50°C for 3 h. Then the reaction mixture was evaporated and for hydrazones (1a–j,l) residue after evaporation was triturated with water (5 mL), precipitate was filtrated, washed with water ($2 \times 3\text{ mL}$) then with diethyl ether ($2 \times 3\text{ mL}$) to give products as solid materials. In case of hydrazone (1k) residue after evaporation was dissolved in water (5 mL) and extracted with chloroform ($2 \times 3\text{ mL}$), organic layer was separated, dried over Na_2SO_4 , evaporated and residue was crystallized from diethyl ether to give product as solid material.

2.2.3. General method for preparation 1,3,4-oxadiazole (2a–l) from *N*-acylhydrazones

Glass tube with rubber-lined cap was evacuated and filled with argon three times. To this tube hydrazone (60 μmol), sulfur (6 mg, 0.18 mmol), K-PHI (5 mg) and acetonitrile (2 mL) were added.

Resulting mixture was stirred at 80°C under irradiation of Blue LED (461 nm, $89.2 \pm 0.26\text{ mW/cm}^2$) for 20 h. Then reaction mixture was cooled to room temperature and centrifuged (1 min at 12,500 rpm), clear solution was separated and solid residue was washed with methanol (2 mL) and centrifuged again. Organic solutions were combined and evaporated to dryness. Residue after evaporation was purified by flash silica gel column chromatography using diethyl ether/dichloromethane (1:2) as an eluent.

3. Results and discussion

K-PHI was characterized by numerous techniques earlier. Therefore here we give only a summary of the most important for photocatalytic applications characteristics of this material.

The surface composition of K-PHI was studied by X-Ray photoelectron spectroscopy (XPS). Carbon in K-PHI exists mostly in C–N (288.2 eV) chemical state along with minor contribution from C–O (286.6 eV) chemical state, due to partial hydrolysis during aqueous treatment (Fig. 2a). Two peaks at 295.9 eV and 293.0 eV are related to K $2p_{1/2}$ and K $2p_{3/2}$ components. In XPS N 1s spectrum peaks after deconvolution at 396.4 eV (C–N⁺–C), 398.6 eV (C–N=C), 400.9 eV (NH_x) and 403.8 eV (N–O) are observed (Fig. 2b). As evidenced by XPS O 1s spectrum the surface of K-PHI is partially covered with OH groups (532.0 eV), deprotonated hydroxyl groups (530.8 eV) and surface adsorbed water (533.3 eV) (Fig. 2c). PXRD pattern of K-PHI matches to the simulated 2D structure reported earlier (Fig. 2d) [31]. Intense peak at 27.2° arises from the stacking of heptazine units in the third dimension that is typical for graphitic carbon nitride. DR (Diffuse reflectance) UV–vis absorption spectrum of K-PHI demonstrates a typical for carbon nitrides absorbance with a band from near-UV to 460 nm assigned to π – π^* transitions as well as broad absorption band up to near-IR that is due to low energetic n – π^* transitions (Fig. 2e) [32,33]. Steady-state photoluminescence (PL) spectrum of K-PHI, recorded at room temperature upon sample excitation with 350 nm photons, shows a maximum at 500 nm (Fig. 2f). The morphology of K-PHI is typical for this material and is represented by ca. 200 nm long rods (Fig. 2g) [15]. From the transmission electron microscopy (TEM) image the well-ordered structure with repeating motives with distances 1.1 nm (diffraction peak at 27.1° in PXRD pattern) and 0.33 nm (diffraction peak at 8.1° in PXRD pattern) can be clearly discerned (Fig. 2h, i) [18].

Oxidative cyclization of *N*'-benzylidenbenzohydrazide 1a to 2,5-diphenyl-1,3,4-oxadiazole 2a by K-PHI has been chosen as a model reaction in order to find the optimal photocatalytic conditions (Scheme 2, Table 1). In the control experiments, without photocatalyst (entry 1) and without light irradiation (entry 2), no oxadiazole 2a was obtained. In all experiments under light irradiation (461 nm, $89.2 \pm 0.26\text{ mW/cm}^2$) in presence of the K-PHI photocatalyst, 2,5-diphenyl-1,3,4-oxadiazole 2a was obtained as the only product. The highest conversion (86%) of the starting hydrazone 1a was observed after 20 h of

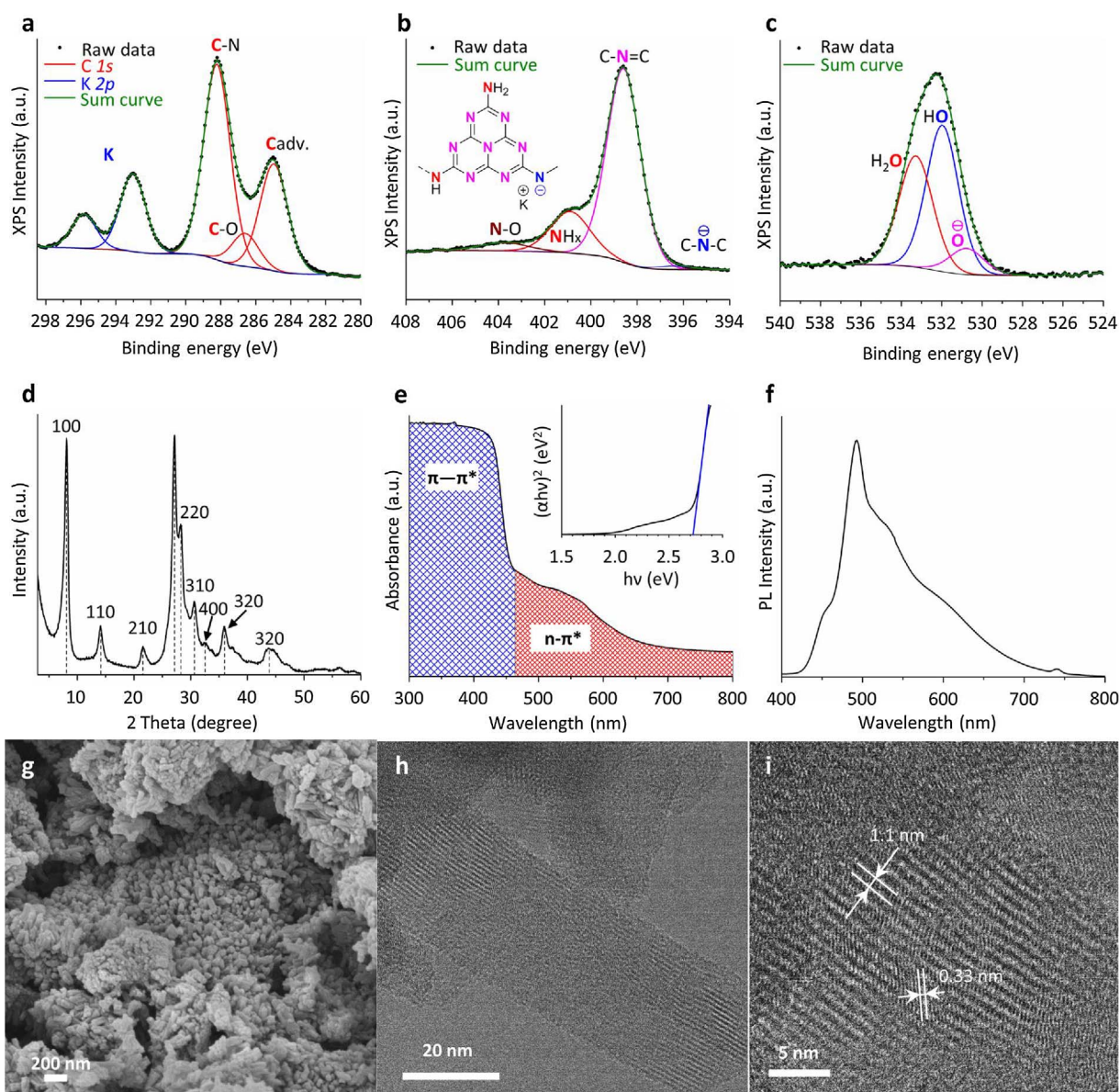
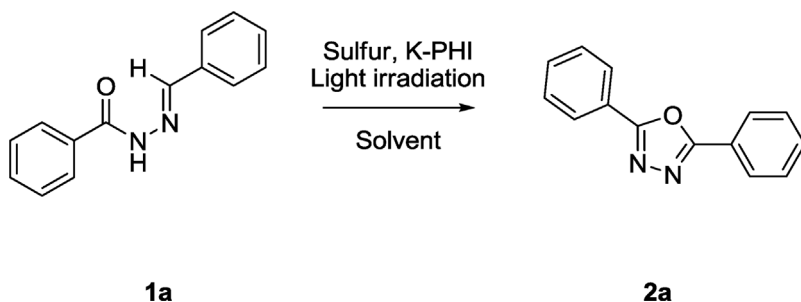


Fig. 2. a) XPS C 1s and K 2p spectra of K-PHI; b) XPS N 1s spectrum of K-PHI; c) XPS O 1s spectrum of K-PHI; d) PXRD pattern of K-PHI with Miller indices adapted from the literature [31]; e) DR UV-vis absorption spectrum of K-PHI with Tauc plot as inset assuming that K-PHI is a direct semiconductor; f) room temperature PL spectrum of K-PHI obtained upon excitation with 350 nm wavelength; g) representative SEM image of K-PHI; h, i) AC-HRTEM images of K-PHI.

irradiation at 80 °C with 3 equivalents of sulfur using acetonitrile as the solvent (entry 6), and it did not improve when the amount of the catalyst was increased (entry 10) (Table S1). Despite quite toxic for other transition metal-based photocatalysts conditions, K-PHI demonstrates excellent stability – even after four cycles conversion of *N'*-benzylidenebenzohydrazide was 80% (entries 7–9). Significantly lower conversions (15–36%) were obtained in less polar solvents: dioxane, benzene,

tert-butanol (entries 3–5), indicating the necessity to stabilize polar transitions states. The conversion of hydrazide **1a** was lowered to 37% (entry 11) and 43% (entry 12), when the reaction was performed without heating and at 50 °C, respectively. This could be explained by the high activation energy of the heterocyclization stage during oxadiazole formation, thus adding a thermal step. Conversion reached only 47%, when oxygen was used as an electron scavenger instead of



Scheme 2. Photocatalytic oxidative cyclization of *N'*-benzylidenebenzohydrazide **1a**.

Table 1

Optimization of the reaction conditions of 2,5-diphenyl-1,3,4-oxadiazole synthesis via *N*-benzylidenebenzohydrazide oxidative cyclization.^a

Exp. No.	Solvent	T, °C	Time, h	Conversion, % ^b
1 ^c	Dioxane or CH ₃ CN	80	20	0
2 ^d	Dioxane or CH ₃ CN	80	20	0
3	Dioxane	80	20	15
4	Benzene	80	20	36
5	<i>t</i> -BuOH	80	20	27
6	CH ₃ CN	80	20	86
7 ^e	CH ₃ CN	80	20	83
8 ^f	CH ₃ CN	80	20	82
9 ^g	CH ₃ CN	80	20	80
10 ^h	CH ₃ CN	80	20	85
11	CH ₃ CN	25	60	37
12	CH ₃ CN	50	20	43
13 ⁱ	CH ₃ CN	80	20	47

^a Reaction conditions: *N*-benzylidenebenzohydrazide (60 μmol), sulfur (0.18 mmol), photocatalyst (5 mg), solvent (2 ml), λ = 461 nm.

^b Conversion was determined by ¹H NMR.

^c Without photocatalyst.

^d Without light irradiation.

^e Second run.

^f Third run.

^g Fourth run.

^h 10 mg of photocatalyst.

ⁱ oxygen as electron scavenger.

sulfur (entry 13), while products of hydrazone **1a** decomposition were observed in ¹H NMR spectra of the reaction mixture, among which benzaldehyde was identified. All in all, this experiment clearly demonstrates that S₈ is more selective electron acceptor than O₂ (see mechanism below for explanation). The structure of K-PHI remains intact after photocatalytic reaction as can be judged from powder X-Ray diffraction patterns and Fourier-transform infrared (FT-IR) spectra (Fig. S2).

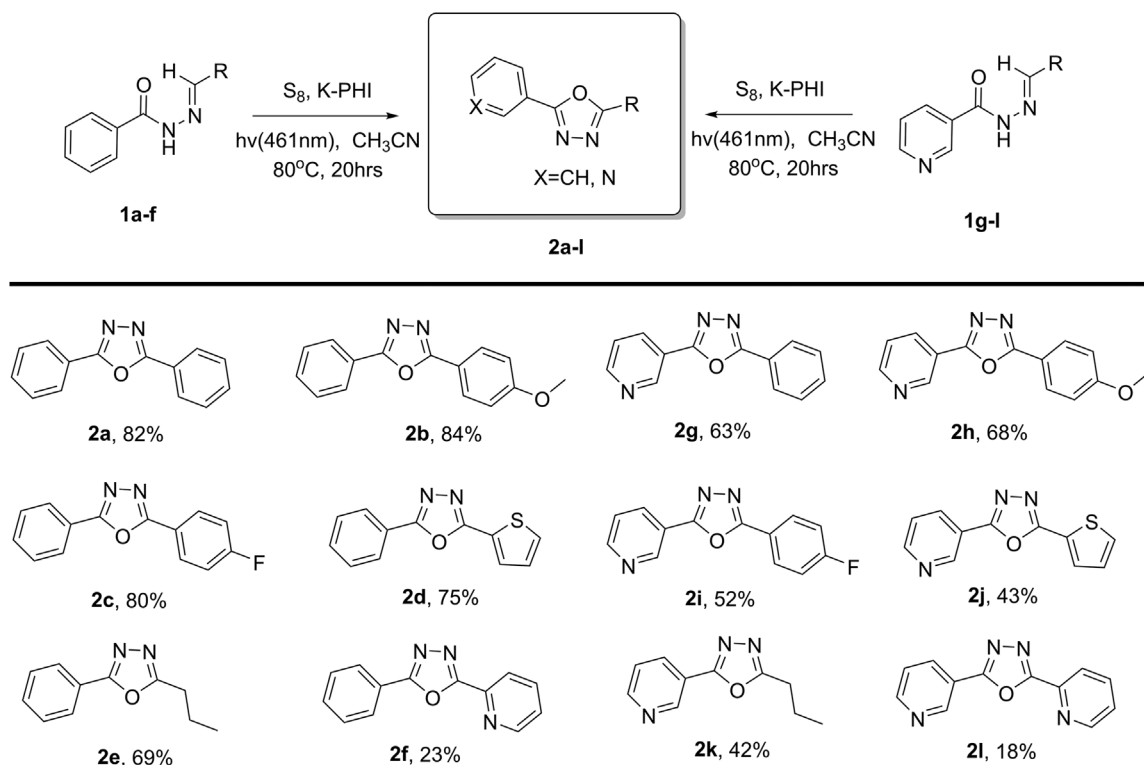
Generally two series of substrates – hydrazones obtained from benzhydrazide (**1a–f**) and nicotinohydrazide derivatives (**1g–l**) – were

selected to estimate the reliability of the proposed approach (Scheme 3). 2-Phenyl-oxadiazoles (**2a–e**) were obtained in good isolated yields (69–84%) regardless the different aromatic or aliphatic character of ylidene-substituent in the starting hydrazones. Moderate yields (42–63%) were observed for oxadiazoles (**2g–l**) originated from nicotinohydrazide. The main reason is electron-accepting nature of the pyridine ring, which as such is a complicated substrate. The pyridine ring withdraws electron density from the carbonyl moiety and hence makes oxygen less reactive toward C=N bond during cyclization (see also below the explanation of the mechanism).

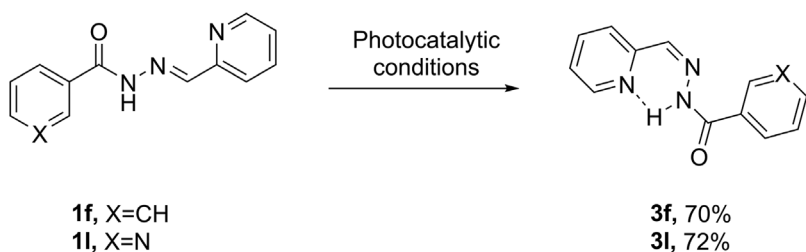
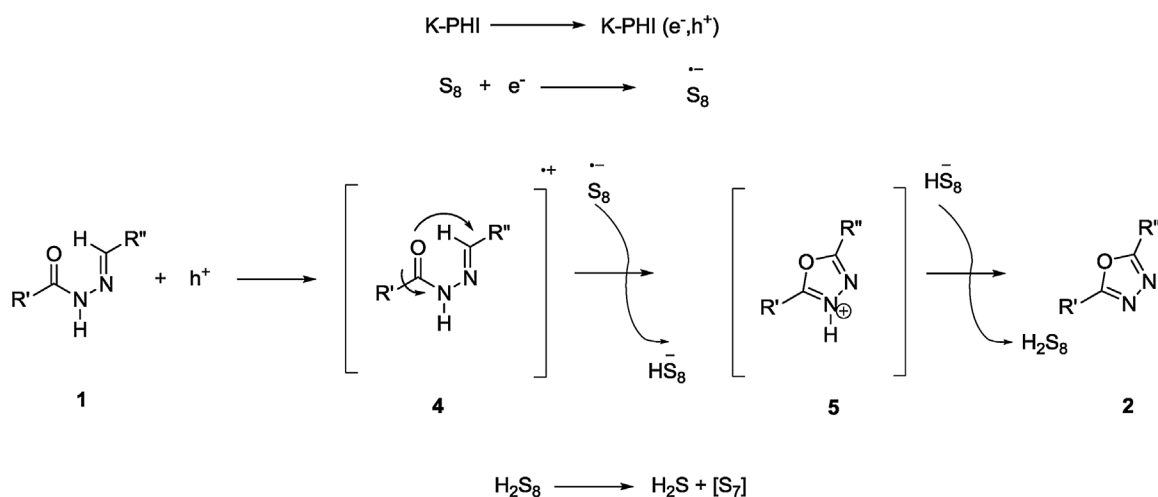
The reaction conditions in *N*-acylhydrazones oxidative cyclization catalyzed by K-PHI in the presence of elemental sulfur can be indeed regarded as very mild as this method also provides previously unknown compounds **2i–l**.

Hydrazones **1f,l** bearing the 2-pyridyl substituent were converted into the corresponding oxadiazoles **2f,l** in only 23% and 18% yields respectively. In order to explain such a special behavior we should point out that, according to the NMR-spectra (SI), all hydrazones, used in this study, were obtained as *E*-isomers. Apparently this configuration is thermodynamically more stable than the *Z*-configuration. However, *E*-hydrazones **1f,l** can undergo isomerization under photocatalytic conditions that leads to the formation of the *Z*-isomer additionally stabilized by hydrogen bonding between NH-moiety and the nitrogen atom in the 2-pyridyl substituent (Scheme 4). Further transformation of *Z*-isomers into the oxadiazoles is significantly more difficult due to the remoteness of the oxygen atom from the C=N electrophilic center. It is interesting that photochemical isomerization of *N*-acylhydrazones was reported earlier, but only under harsh UV-irradiation [34,35]. Our preliminary study suggests that K-PHI also mediates this type of isomerization process.

A tentative mechanism of photocatalytic 1,3,4-oxadiazole synthesis is depicted in Scheme 5. Irradiation of K-PHI with the visible light creates photogenerated electrons (e⁻) and holes (h⁺), which are located at the conduction and valence band of the photocatalyst, respectively. *N*-Acylhydrazone is oxidized by the hole to the radical-cation **4** while sulfur removes the electron from the conduction band of K-



Scheme 3. Photocatalytic preparation of 2,5-disubstituted-1,3,4-oxadiazoles **2a-l** from hydrazones **1a-l**.

Scheme 4. Photocatalytic isomerization of *N*-acylhydrazones.

Scheme 5. Possible mechanism of photocatalytic 1,3,4-oxadiazole synthesis.

PHI and is converted into the $S_8^{\cdot-}$ radical-anion [36]. Based on several reported mechanisms of oxidative cyclization reactions we assume that intermediate **4** is converted into protonated oxadiazole **5** via proton coupled electron transfer (PCET) from aldimine moiety ($-CH=N-$) to sulfur radical anion ($S_8^{\cdot-}$) that is transformed into hydrosulfide anion (HS_8^-) [28,30,37]. At the last stage, removal of proton from oxadiazolium cation **5** by HS_8^- leads to target oxadiazole **2** and H_2S_8 . H_2S_8 is apparently unstable and is decomposed into H_2S (was confirmed as Ag_2S by passing the reaction mixture gases through $AgNO_3$ solution) and presumably S_7 , which again acts as electron/proton acceptor, similarly to S_8 .

Based on the behavior of hydrazones **1f**, **1l**, the hydrazone *E*-configuration is decisive for this reaction. On the contrary, in the hydrazone *Z*-configuration, the oxygen atom is far from the reaction center, which practically inhibits the already disfavored 5-*endo*-trig cyclization process [38].

Having the mechanism of 1,3,4-oxadiazole photooxidation, selective behavior of S_8 in this process can be explained. Acting as electron acceptors, both oxygen and sulfur are reduced to their radical anions, $S_8^{\cdot-}$ and $O_2^{\cdot-}$ respectively. Among these two, $O_2^{\cdot-}$ is known to be a strong nucleophile [39]. Once formed, it readily attacks $C=N$ bond in *N*-acylhydrazone radical cation **4** followed by its cleavage with the recovery of the starting aldehyde. This is not the case for $S_8^{\cdot-}$ as can be concluded from higher selectivity of *N*-acylhydrazone oxidation mediated by elemental sulfur (compare entries 6 and 13, Table 1). $S_8^{\cdot-}$ is effectively turned into HS_8^- via PCET from *N*-acylhydrazone radical cation.

Despite the photocatalyst activates *N*-acylhydrazone and S_8 to their more reactive radical species, and hence initiates 1,3,4-oxadiazole synthesis, temperature is still beneficial to speed up cyclization of **4** to **5** and to improve desorption of the product from the photocatalyst surface, but nonetheless it is not critical for the process as 1,3,4-oxadiazoles can be prepared at room temperature running the process for extended time (Table 1, entry 11). Shown here efficacy of K-PHI for the photooxidative formation of 1,3,4-oxadiazoles under mild conditions

can to our opinion be further extended onto reactions involving other heterocyclic substrates.

4. Conclusion

Potassium poly(heptazine imide), a carbon nitride based heterogeneous photocatalyst, opens a convenient route to synthesize 2,5-disubstituted-1,3,4-oxadiazoles via oxidative cyclization of the corresponding *N*-acylhydrazones. This transformation was accomplished under visible light irradiation (461 nm, $89.2 \pm 0.26 \text{ mW cm}^{-2}$) using elemental sulfur as a cheap and selective electron scavenger. Twelve different 1,3,4-oxadiazoles with aryl, hetaryl and alkyl substituents were obtained with 84–18% isolated yield. The mechanism of this transformation was investigated, and it was found that *trans*-configuration at the aldimine moiety is crucial for the cyclization to proceed. The *trans*-*N*-acylhydrazones, bearing 2-pyridyl substituent, under the photocatalytic conditions can, however, be also easily photoisomerized to the corresponding *cis*-isomers. In the presence of a pyridyl moiety, these isomers are well stabilized by the intramolecular H-bonding and hence averse to cyclization.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.01.072>.

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